913

STANDARDS DEVELOPMENT BRANCH OMOE
3 6936 00000 2254

THE FORM OF MERCURY IN FRESHWATER FISH

May 1974

QP
82.2
.M4
B56
1974
MOE

Ontario

Ministry
of the
Environment

The Honourable
George A. Kerr, Q.C.,
Minister

Everett Biggs,
Deputy Minister

Copyright Provisions and Restrictions on Copying:

This Ontario Ministry of the Environment work is protected by Crown copyright (unless otherwise indicated), which is held by the Queen's Printer for Ontario. It may be reproduced for non-commercial purposes if credit is given and Crown copyright is acknowledged.

It may not be reproduced, in all or in part, part, for any commercial purpose except under a licence from the Queen's Printer for Ontario.

For information on reproducing Government of Ontario works, please contact Service Ontario Publications at copyright@ontario.ca

QP
82.2 M4
B56
1974

THE FORM OF MERCURY IN FRESHWATER FISH

J. N. Bishop and B. P. Neary

Inorganic Trace Contaminants Laboratory, Ministry of the Environment, Toronto, Ontario, Canada.

Nearly 600 fish representing 16 species were analyzed for methyl and total mercury. The average methyl to total mercury ratio is 88.9%, indicating that essentially all of the mercury in fish muscle is present as methyl mercury. The effect of age, weight and length on the methyl/total mercury ratio is examined. These variables have no significant effect on the ratio. The ratio is similar for the sizes, ages, and species of fish examined.

I. INTRODUCTION

The toxicity of methyl mercury has been well documented (1). Fish with elevated concentrations of mercury (up to 28 ppm) have been found in several areas of North America, and there has been serious concern that a considerable portion of this mercury

HAZARDOUS CONTAMINANTS
AND STANDARDS BRANCH
135 ST. CLAIR AVENUE WEST
TORONTO, ONTARIO M4V 1P5

exists in the methyl form in fish tissue.

There have been a number of papers published on the ratio of methyl to total mercury (MeHg/Tot Hg) in fish tissue, and disagreement between laboratories concerning this ratio has been expressed. A number of researchers have reported that essentially all of the mercury in fish muscle is in the methyl form (2-16). Others have reported ratios varying from 0-75% (17), but their analytical methodology has been criticized (18, 19). Bache et al., (20) reported that the proportion of methyl mercury to total mercury increases with age, however,their data is based on analysis of whole ground fish and has been questioned by Westöö (21). There does appear to be one marine species, Pacific Blue Marlin, which for reasons not presently understood, has a low methyl to total mercury ratio. The ratio of 25% reported by Rivers et al., (20) has been confirmed by other analysts (21).

The Ontario Ministry of the Environment (MOE) has been involved in the analysis of fish for mercury since 1969, and has analyzed over 25,000 fish for total mercury. A substantial portion of these were analyzed for methyl mercury as well. The current study involves only a small portion of these samples, representing a three month period in 1973. These fish, over 500 altogether, were analyzed for both total and methyl mercury. The methyl mercury to total mercury ratio was calculated, and the effect on the ratio of age, length, and species was also examined.

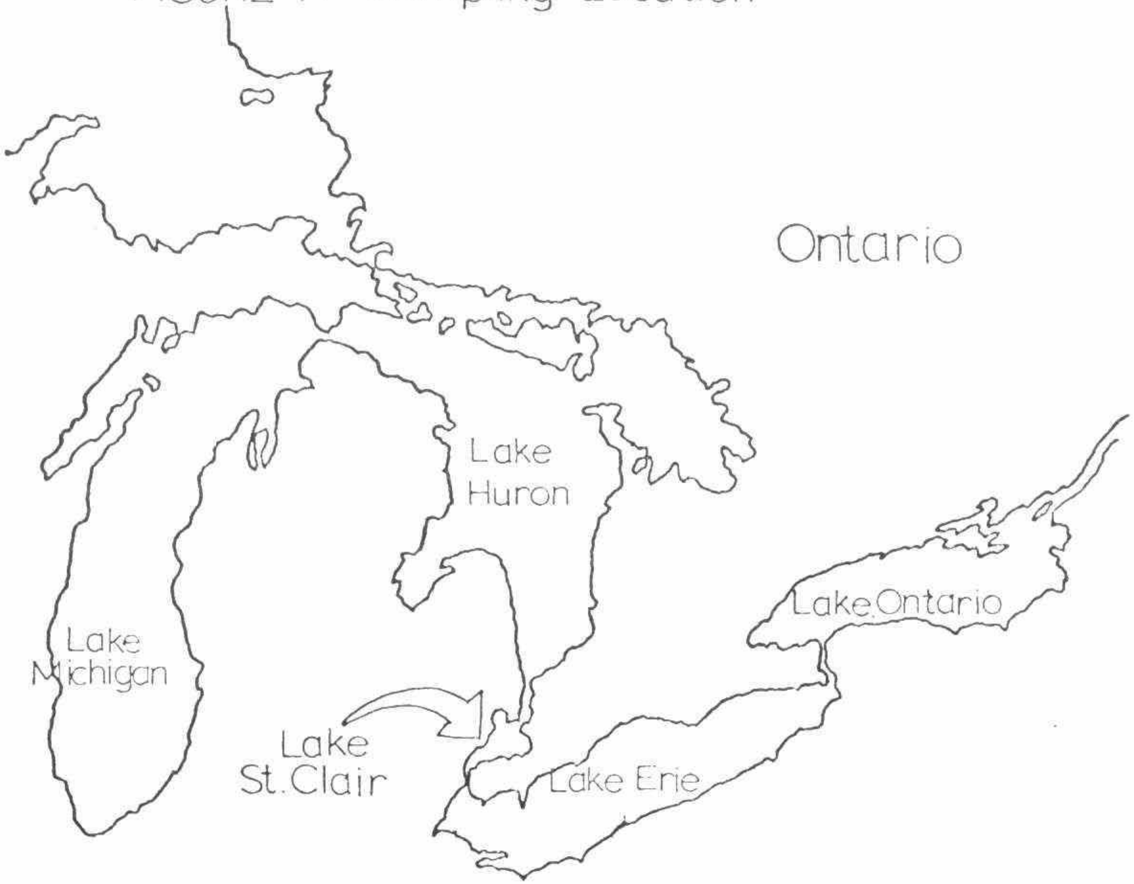
II. EXPERIMENTAL

A. Analytical

Approximately 580 fish from the Lake St. Clair system (see Fig. 1) were captured, immediately frozen, and submitted for analysis. After thawing, the fish were sampled to provide about five grams of epaxial musculature.

The flesh was well homogenized and subsamples were analyzed for methyl mercury and total mercury using methods modified from those of Rudling (22) and Hatch and Ott (23).

FIGURE 1: Sampling Location



B. Statistical

The analytical results reported in this study were drawn from a larger group of data, and represented 16 species, for each of which there were more than 10 specimens. The species data populations were investigated for normality, and all relationships were examined by the use of product moment correlation coefficients. All calculations were done according to methods outlined in Sokal & Rohlf (24) on a Hewlett-Packard 9810A programmable calculator.

III. RESULTS

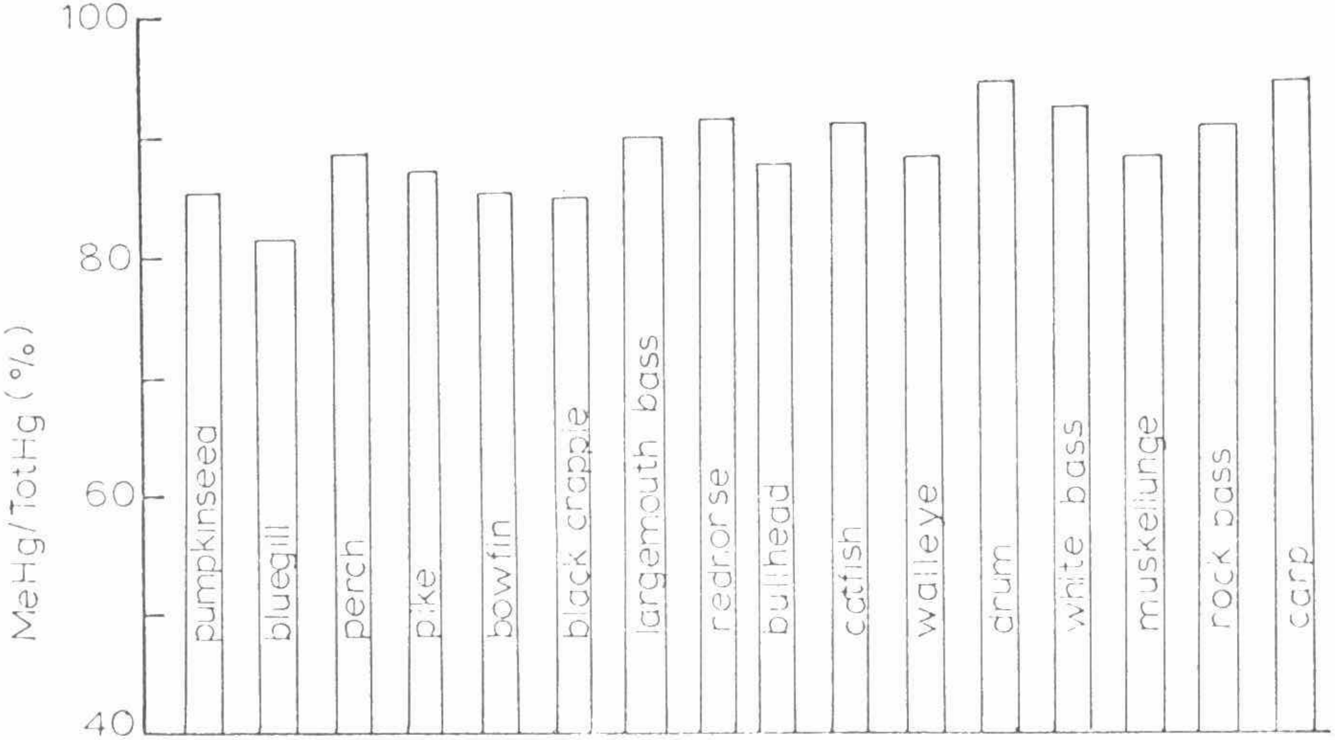
A. Total and Methyl Mercury Data and MeHg/Tot Hg Ratios.

Methyl and total mercury data and the MeHg/Tot Hg ratios are shown in Table I and Figure 2. Table I also lists the species examined, the number of specimens for each species, and the ranges for the methyl and total mercury data. This table also illustrates the range among species for total and methyl mercury concentrations, and it shows the

TABLE I: MERCURY DATA

Species	n	Total Hg Range (ppm)	Methyl Hg Range (ppm)	MeHg/Tot Hg Ratio %
Pumpkinseed	22	1.10-2.80	0.97-2.40	84.8±9.8%
Bluegill	36	0.58-3.20	0.49-2.80	81.8±8.7%
Perch	65	0.13-3.30	0.10-3.20	89.0±11.0%
N. Pike	69	1.80-9.90	1.60-8.95	86.8±11.0%
Bowfin	16	0.51-11.6	0.47-7.60	85.4±14.0%
B. Crappie	36	0.79-3.70	0.64-3.30	85.4±7.9%
LM Bass	14	1.04-4.12	1.07-3.87	90.2±10.0%
N. Redhorse	28	0.07-5.16	0.07-5.00	92.1±8.0%
Y. Bullhead	27	0.62-4.88	0.52-4.00	86.9±7.9%
Channel Cat	11	1.05-3.94	0.99-3.55	92.0±7.6%
Y. Walleye	97	0.27-5.80	0.29-4.50	88.5±12.0%
F.W. Drum	22	0.11-1.89	0.11-1.68	95.1±7.1%
White Bass	27	0.44-3.35	0.38-3.58	93.2±10.0%
Muskie	13	1.08-23.3	0.92-20.4	88.0±6.6%
Rock Bass	63	0.22-4.25	0.16-4.21	92.1±8.2%
Carp	30	0.31-2.90	0.25-2.70	95.3±10.0%

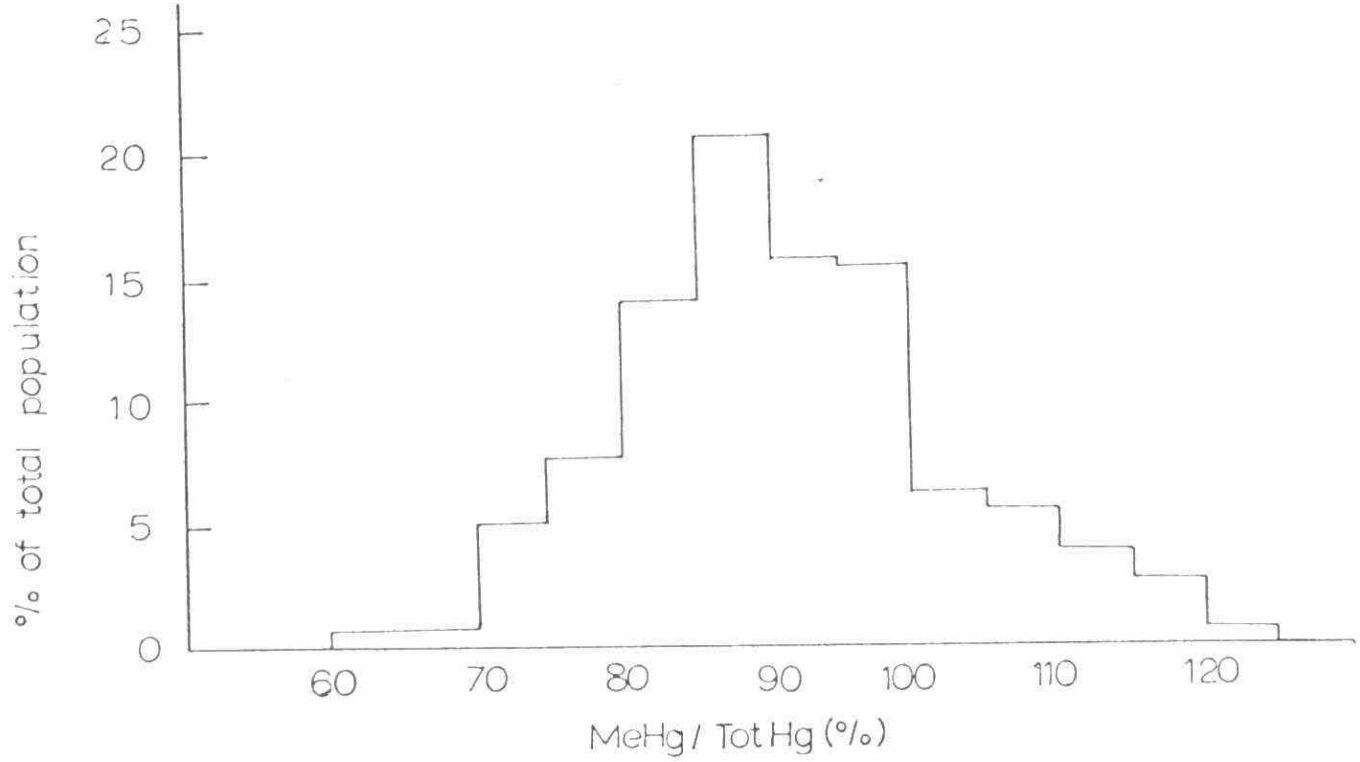
FIGURE 2: MeHg/Tot Hg by Species



similarity in MeHg/Tot Hg ratios for all species. For example, the total mercury concentration in muskellunge ranges from 1 ppm to 23 ppm, but the MeHg/Tot Hg ratio is around 90%. For perch, total mercury concentrations range from very low to about 3.3 ppm, but again the MeHg/Tot Hg ratio remains at 90%. Figure 2 shows the MeHg/Tot Hg ratio by species, and it illustrates the similarity of ratios from one species to another. It can be seen that the ratios range from 82 to 96% as methyl mercury.

Figure 3 illustrates the distribution of individual MeHg/Tot Hg ratios. All results were plotted in this histogram, and it shows clearly that the vast majority of the ratios fall between 80% and 100%. The histogram also shows a few fish whose methyl mercury content appears to be higher than 100% of the total mercury. It should be pointed out that some error is associated with both methyl and total mercury analyses, and this histogram is affected by the cumulative error.

FIGURE 3: Distribution of Ratios



Furthermore, most of these values were from fish with extremely low mercury content, so that analytical errors would have a more noticeable effect.

B. Effect of Length, Weight and Age on MeHg/Tot Hg Ratios.

Correlation coefficients between the methyl to total mercury ratio and fish length were calculated for all sixteen species, and these results are shown in Table II. The length and weight of the fish are highly correlated, and the MeHg/Tot Hg versus weight correlations were very similar to those shown for the MeHg/Tot Hg versus length correlations (Table II). For two species (Perch and Yellow Walleye), age determinations were done, but there was no significant relationship between age and the methyl to total mercury ratio ($r = 0.032$ for Perch and $r = 0.061$ for Yellow Walleye). This examination was prompted by claims that the ratio increased as the fish grew older and larger. Clearly, these data indicate no correlation between length and the MeHg/Tot Hg ratio.

TABLE II: CORRELATION DATA: Coefficients.

Species	Methyl/mercury vs Total Mercury	MeHg/Tot Hg Ratio vs Length
Pumpkinseed	0.900	-0.129
Bluegill	0.938	-0.343
Perch	0.991	0.224
N. Pike	0.935	0.161
Bowfin	0.969	-0.280
B. Crappie	0.957	0.082
LM Bass	0.933	0.095
N. Redhorse	0.997	-0.507
Y. Bullhead	0.982	0.048
Channel Cat	0.984	-0.546
Y. Walleye	0.982	0.062
F.W. Drum	0.986	0.045
W. Bass	0.983	-0.103
Muskellunge	0.999	0.104
R. Bass	0.992	0.073
Carp	0.958	-0.008

For one species (Northern Redhorse) the correlation is significantly different from zero, but even in this case there is no indication of a meaningful relationship between length and the MeHg/Tot Hg ratio.

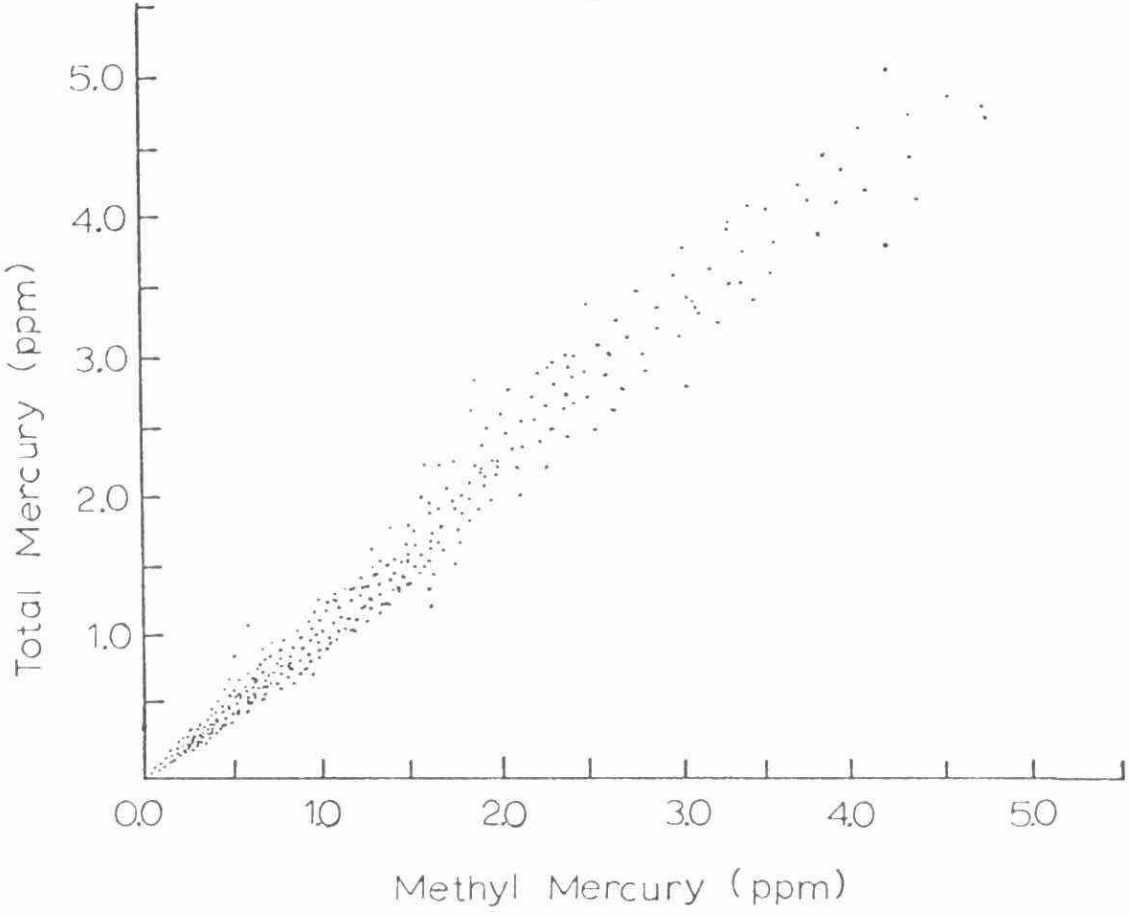
Table II also shows the excellent correlations, for all species, between methyl mercury and total mercury concentration.

The overall relationship between methyl and total mercury for all specimens is shown on Figure 4.

IV. DISCUSSION AND CONCLUSIONS

It is obvious that the conclusions from such a study are highly dependent on analytical precision and accuracy. Accordingly, strict quality control measures were enforced. Spiking studies based on the addition of known amounts of methyl mercuric chloride to homogenized fish established 95±3% and 89±10% as the average recoveries of the total and methyl mercury methods, respectively. Replicate analyses of "control" fish - fish whose methyl and

FIGURE 4: Methyl & Total Mercury



total mercury concentration has been established by analyzing them at least 50 times - indicated 6% and 7% as the relative precision of the two methods. Accordingly, neither methyl nor total mercury results were corrected for recovery. Standard reference materials such as USBS Orchard Leaves 1571, Bovine Liver 1577, and Kodak's Gelatin Standards 11624, 11626, 11628(25), were also analyzed and yielded a recovery of 96 to 99%. Analytical quality of the methods was further monitored by successfull participation in numerous round robin studies throughout this project.

Several conclusions can be drawn from the data presented. For the 16 species examined, the average MeHg/Tot Hg ratio ranges from about 82% to 95%, with a mean of 88.9±7%. This value firmly supports the conclusions of other researchers that essentially all of the mercury present in fish muscle is in the methyl form.

The proportion of mercury present as methyl mercury in fish muscle is independent of fish age, weight, or length.

There appear to be no significant differences between the MeHg/Tot Hg ratios for any of the sixteen species of fish examined. While there may be freshwater fish with lower MeHg/Tot Hg ratios, none were encountered in this study.

REFERENCES

1. Kurland, L.T. World Neurology, 2 370 (1961).

2. Westöö, G., Acta. Chem. Scand., 20 2131 (1966).

3. Westöö, G., Acta. Chem. Scand., 21 1790 (1967).

4. Noren, K., Westöö, G., Var Foda (1967) 138.

5. Sumino, K., Kobe, J., Med. Sci., 14 115 (1968).

6. Rydalv, M., Westöö, G., Var Foda (1969) 20.

7. Zitko, V., et al., J. Fish. Res. Board (Canada) 28 1285 (1971).

8. Sumner, A.K., Saha, J.G., Env. Lett., 2 167 (1971).

9. Uthe, J.F., Solomon, J., Grift, B., J.A.O.A.C., 55 583 (1972).

10. Lockhart, W.L., Uthe, J.F., Kenney, A.R., Mehrle, P.M., J. Fish. Res. Board (Canada) 29 1519 (1972).

11. Thomas, R.J., Hagstrom, R.A., Kuchar, E.J. Anal. Chem., 44 512 (1972).

12. Fukui, S., et al., "Advances in Water Pollution Research" p.819, Pergamon Press, 1973.

13. Weissberg, B.G., Zobel, M.G.R., Bull. Env. Cont. Toxicol., 9 148 (1973).

14. Kleinert, S.J., Degurse, P.E., Technical Bulletin No.52, Dept. Natural Resources, Madison, Wisconsin, 1972.

15. Smith, J.C., et al., Fed. Proc., 30 221 (1971). (Abstracts only) and Smith J.C., personal communication, 1973.

16. Kamps, L.R., et al., Bull. Env. Cont. Toxicol., 8 273 (1972).

17. Ui, J., Rev. Intern. Oceanogr. Med., 23 79 (1971).

18. Berglund, F., et al., Nordforsk Hygienisk Tidskrift, Supplementum 4, Stockholm 1971.

19. Westöö, G., "Heavy Metals in the Aquatic Environment" Nashville, Tennessee, December 1973.

20. Rivers, J.B., et al., Bull Env. Cont. Toxicol. 8 257 (1972).

21. Westöö, G., personal communication.

22. Rudling, L., Institutet for Vatten-och Luftvardsforskning, Stencil C7A, Stockholm, Sweden, 1970.

23. Hatch, W.R., Ott, W.L. Anal. Chem., 40 2085 (1968).

24. Sokal, R.R., Rohlf, F.J., "Biometry" W.H. Freeman and Co., (San Francisco, 1969).

25. Anderson, D.H., Murphy, J.J. and White W.W. "Anal. Chem. 44 2099-2100 (1972).

QP
82.2
.M4
B56
1974